

FORM PTO-1390  
(REV 10-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

B-4208PCT 618872-5

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)  
not yet assigned 09/868227INTERNATIONAL APPLICATION NO.  
PCT/KR99/00798INTERNATIONAL FILING DATE  
21 December 1999PRIORITY DATE CLAIMED  
22 December 1998

TITLE OF INVENTION MICROPOROUS SOLID ELECTROLYTES AND METHODS FOR PREPARING THEM

APPLICANT(S) FOR DO/EO/US (1) Dong Hun JANG (2) Sa Heum KIM (3) Han Jun KIM  
(4) Sung Min HONG

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)).
4. ☒ The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(3)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11 to 16 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.  
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

copy of PCT International Application as published consisting of:

Title page with Abstract, Specification, Claims, and International Search Report

copy of 3 sheets of Drawings as filed (Figs. 1-3)

Claim to Priority

copy of Submission of Amendments under Article 34

copy of Form PCT/IB/308

copy of PCT Demand

copy of Form PCT/IB/332

copy of Form PCT/IB/301

copy of Form PCT/IB/304

09/868227

17. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**

Neither international preliminary examination fee (37 CFR 1.482)  
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO  
and International Search Report not prepared by the EPO or JPO ..... \$1000.00

International preliminary examination fee (37 CFR 1.482) not paid to  
USPTO but International Search Report prepared by the EPO or JPO. .... \$860.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but  
international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$710.00

International preliminary examination fee paid to USPTO (37 CFR 1.482)  
but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$690.00

International preliminary examination fee paid to USPTO (37 CFR 1.482)  
and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00

**ENTER APPROPRIATE BASIC FEE AMOUNT =****CALCULATIONS** PTO USE ONLY

PCT/PTO 1 5 JUN 2001

\$ 1000.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	9 - 20 =	0	X \$18.00
Independent claims	2 - 3 =	0	X \$80.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable) 0*			+ \$270.00

\$ 0

\$ 0

\$ 0

**TOTAL OF ABOVE CALCULATIONS =**

\$ 1000.00

☒ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above  
are reduced by 1/2.

\$ 500.00

**SUBTOTAL =**

\$ 500.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$

+

**TOTAL NATIONAL FEE =**

\$ 500.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be  
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property

\$

+

**TOTAL FEES ENCLOSED =**

\$ 500.00

\*PRELIMINARY AMENDMENT DELETING  
MULTIPLE DEPENDENCIES ENCLOSED.

Amount to be  
refunded:

\$

charged:

\$

a. ☒ A check in the amount of \$ 500.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees.  
A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any  
overpayment to Deposit Account No. 12-0415. A duplicate copy of this sheet is enclosed.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR  
1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

June 15, 2001  
DATE

LADAS & PARRY  
5670 Wilshire Blvd., #2100  
Los Angeles, California 90036-5679  
Telephone No.: (323) 934-2300  
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SIGNATURE:

Mavis S. Gallenson

NAME

32,464

REGISTRATION NUMBER

07/868227

JC18 Rec'd PCT/PTO 1 5 JUN 2001

EL652175763US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Dong Hun JANG, et al.) Re: Preliminary Amendment  
)  
U.S. Appln. No.: not yet ) Group: not yet assigned  
assigned )  
)  
U.S. Filing Date: concurrently ) Examiner: not yet assigned  
herewith )  
)  
International Application No: )  
PCT/KR99/00798 )  
)  
International Filing Date: )  
21 December 1999 ) Our Ref.: B-4208PCT 618872-5  
)  
For: "MICROPOROUS SOLID )  
ELECTROLYTES AND METHODS )  
FOR PREPARING THEM" ) Date: June 15, 2001

Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Attn: United States Designated/Elected Office (DO/EO/US)

Sir:

Prior to examination of the above-identified application, it is respectfully requested that the following amendments be made to the claims and the drawings:

IN THE CLAIMS

Please replace Claims 4 and 5 with new amended Claims 4 and 5, which are set forth below. (Appendix A, which is enclosed herewith, shows how Claims 4 and 5 were amended to produce new amended Claims 4 and 5.)

4. (amended) A solid electrolyte for rechargeable cells according to Claim 2, in which

said solid electrolyte is prepared by an activation procedure in which an ion conductive liquid electrolyte is absorbed into said electrolyte film, and

said ion conductive liquid electrolyte is obtained by dissolving one or two or more lithium salts selected from the group consisting of LiClO<sub>4</sub>, LiBF<sub>4</sub>, LiPF<sub>6</sub>, LiAsF<sub>6</sub>, LiSCN, LiCF<sub>3</sub>SO<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> and LiC(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub> in a mixture of one or two or more organic solvents selected from the group consisting of ethylene carbonate, propylene carbonate, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, g-butyrolactone, 1,3-dioxane, tetrahydrofuran, 2-methyltetrahydrofuran, dimethylsulfoxide, sulfolane, N,N-dimethylformamide, diglyme, triglyme and tetraglyme in a concentration of 0.5M to 2M.

5. (Amended) A solid electrolyte for rechargeable cells according to Claim 2, in which

said absorbent is a mixture of one or two or more selected from the group consisting of porous polymer particles such as polyethylene, polypropylene, polystyrene, polyurethane, pulp, cellulose, cork and wood powder; mineral particles such as clay, paragonite, montmorillonite and mica; synthetic oxide compounds particles such as zeolite, porous silica and porous alumina; mesoporous molecular sieves having 2 to 30 nm of pore diameter made of oxide compounds or polymers; and other commercially available absorbents;

said polymer binder is a mixture of one or two or more selected from the group consisting of copolymers of polyvinylidene fluoride, vinylidene fluoride and hexafluoropropylene, copolymers of vinylidene fluoride and maleic anhydride, polyvinylchloride, polymethylmethacrylate, polymethacrylate, cellulose triacetate, polyurethane, polysulfone, polyether, polyethylene, polypropylene, polyethylene oxide, polyisobutylene, polybutylidene, polyvinylalcohol, polyacrylonitrile, polyimide, polyvinyl formal, acrylonitrilebutyldiene rubber, ethylene-propylene-diene-monomer, tetraethyleneglycol diacrylate, polydimethylsiloxane, polycarbonate and silicon polymer, or their copolymer;

said solvent for dissolving polymer binders is a mixture of one or two or more solvents selected from the group consisting of N-methylpyrrolidinone, dimethylformamide, dimethylacetamide, tetrahydrofuran, acetonitrile, cyclohexanone, chloroform, dichloromethane, hexamethylphosphoramide, dimethylsulfoxide, acetone and dioxane; and

said non-solvent for the polymer binders is a mixture of one or two or more selected from the group consisting of water, ethanol, ethylene glycol, glycerol, acetone, dichloromethane, ethylacetate, butanol, pentanol, hexanol and ether.

Please add the following new claims:

8. (New) A solid electrolyte for rechargeable cells according to Claim 3, in which

said solid electrolyte is prepared by an activation procedure in which an ion conductive liquid electrolyte is absorbed into said electrolyte film, and

said ion conductive liquid electrolyte is obtained by dissolving one or two or more lithium salts selected from the group consisting of  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSCN}$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_2$  and  $\text{Li}(\text{CF}_3\text{SO}_2)_3$  in a mixture of one or two or more organic solvents selected from the group consisting of ethylene carbonate, propylene carbonate, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate,  $\gamma$ -butyrolactone, 1,3-dioxane, tetrahydrofuran, 2-methyltetrahydrofuran, dimethylsulfoxide, sulfolane, N,N-dimethylformamide, diglyme, triglyme and tetraglyme in a concentration of 0.5M to 2M.

9. (New) A solid electrolyte for rechargeable cells according to Claim 3, in which

said absorbent is a mixture of one or two or more selected from

the group consisting of porous polymer particles such as polyethylene, polypropylene, polystyrene, polyurethane, pulp, cellulose, cork and wood powder; mineral particles such as clay, paragonite, montmorillonite and mica; synthetic oxide compounds particles such as zeolite, porous silica and porous alumina; mesoporous molecular sieves having 2 to 30 nm of pore diameter made of oxide compounds or polymers; and other commercially available absorbents;

said polymer binder is a mixture of one or two or more selected from the group consisting of copolymers of polyvinylidene fluoride, vinylidene fluoride and hexafluoropropylene, copolymers of vinylidene fluoride and maleic anhydride, polyvinylchloride, polymethylmethacrylate, polymethacrylate, cellulose triacetate, polyurethane, polysulfone, polyether, polyethylene, polypropylene, polyethylene oxide, polyisobutylene, polybutylidene, polyvinylalcohol, polyacrylonitrile, polyimide, polyvinyl formal, acrylonitrilebutyldiene rubber, ethylene-propylene-diene-monomer, tetraethyleneglycol diacrylate, polydimethylsiloxane, polycarbonate and silicon polymer, or their copolymer;

said solvent for dissolving polymer binders is a mixture of one or two or more solvents selected from the group consisting of N-methylpyrrolidinone, dimethylformamide, dimethylacetamide, tetrahydrofuran, acetonitrile, cyclohexanone, chloroform, dichloromethane, hexamethylphosphoramide, dimethylsulfoxide, acetone and dioxane; and

said non-solvent for the polymer binders is a mixture of one or two or more selected from the group consisting of water, ethanol, ethylene glycol, glycerol, acetone, dichloromethane, ethylacetate, butanol, pentanol, hexanol and ether.

Re: Preliminary Amendment  
June 15, 2001  
Page 5

IN THE DRAWINGS

The drawings (Figs. 1-3) as filed in PCT International Application No. PCT/KR99/00798 were attached to the subject PCT application due to a clerical error; and therefore the drawings were amended during International Preliminary Examination (IPE) under Article 34. A copy of the amended drawings is attached.


It is respectfully requested that the attached drawings (Figs. 1-3), amended during International Preliminary Examination (IPE) under Article 34, be entered into the prosecution history of the subject application.

REMARKS

This Preliminary Amendment amends Claims 4 and 5 to produce new amended Claims 4 and 5, which are not multiply dependent. Claims 8 and 9 were added to provide similar coverage. Once examination on the merits has begun, the Applicant may elect to amend new amended Claims 4 and 5 to make this claim multiply dependent or to add additional claims to this application to provide coverage similar to, broader than, or narrower than the present claims.

Amendment of the subject application is respectfully requested.

Respectfully submitted,

  
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Enclosures: Appendix A (2 pages)  
copy of IPE amended drawings (Figs. 1-3) (2 sheets)

Appendix A

(VERSION WITH MARKINGS TO SHOW CHANGES)

Page 1 of 2

Please amend the claims as follows:

4. (amended) A solid electrolyte for rechargeable cells according to Claim 2 (or Claim 3), in which

said solid electrolyte is prepared by an activation procedure in which an ion conductive liquid electrolyte is absorbed into said electrolyte film, and

said ion conductive liquid electrolyte is obtained by dissolving one or two or more lithium salts selected from the group consisting of  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSCN}$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  and  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$  in a mixture of one or two or more organic solvents selected from the group consisting of ethylene carbonate, propylene carbonate, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate,  $\gamma$ -butyrolactone, 1,3-dioxane, tetrahydrofuran, 2-methyltetrahydrofuran, dimethylsulfoxide, sulfolane, N,N-dimethylformamide, diglyme, triglyme and tetraglyme in a concentration of 0.5M to 2M.



## Appendix A

## (VERSION WITH MARKINGS TO SHOW CHANGES)

Page 2 of 2

5. (Amended) A solid electrolyte for rechargeable cells according to Claim 2 (or Claim 3), in which

said absorbent is a mixture of one or two or more selected from the group consisting of porous polymer particles such as polyethylene, polypropylene, polystyrene, polyurethane, pulp, cellulose, cork and wood powder; mineral particles such as clay, paragonite, montmorillonite and mica; synthetic oxide compounds particles such as zeolite, porous silica and porous alumina; mesoporous molecular sieves having 2 to 30 nm of pore diameter made of oxide compounds or polymers; and other commercially available absorbents;

said polymer binder is a mixture of one or two or more selected from the group consisting of copolymers of polyvinylidene fluoride, vinylidene fluoride and hexafluoropropylene, copolymers of vinylidene fluoride and maleic anhydride, polyvinylchloride, polymethylmethacrylate, polymethacrylate, cellulose triacetate, polyurethane, polysulfone, polyether, polyethylene, polypropylene, polyethylene oxide, polyisobutylene, polybutylidene, polyvinylalcohol, polyacrylonitrile, polyimide, polyvinyl formal, acrylonitrilebutyldiene rubber, ethylene-propylene-diene-monomer, tetraethyleneglycol diacrylate, polydimethylsiloxane, polycarbonate and silicon polymer, or their copolymer;

said solvent for dissolving polymer binders is a mixture of one or two or more solvents selected from the group consisting of N-methylpyrrolidinone, dimethylformamide, dimethylacetamide, tetrahydrofuran, acetonitrile, cyclohexanone, chloroform, dichloromethane, hexamethylphosphoramide, dimethylsulfoxide, acetone and dioxane; and

said non-solvent for the polymer binders is a mixture of one or two or more selected from the group consisting of water, ethanol, ethylene glycol, glycerol, acetone, dichloromethane, ethylacetate, butanol, pentanol, hexanol and ether.

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(Amendments)

## DRAWINGS

Fig. 1

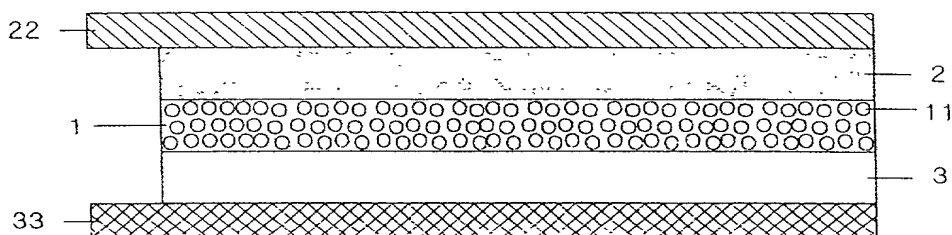


Fig. 2

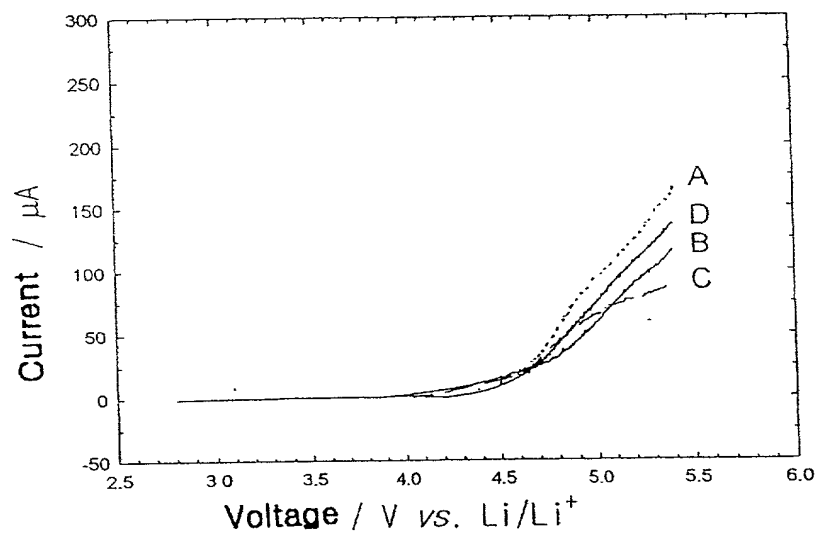
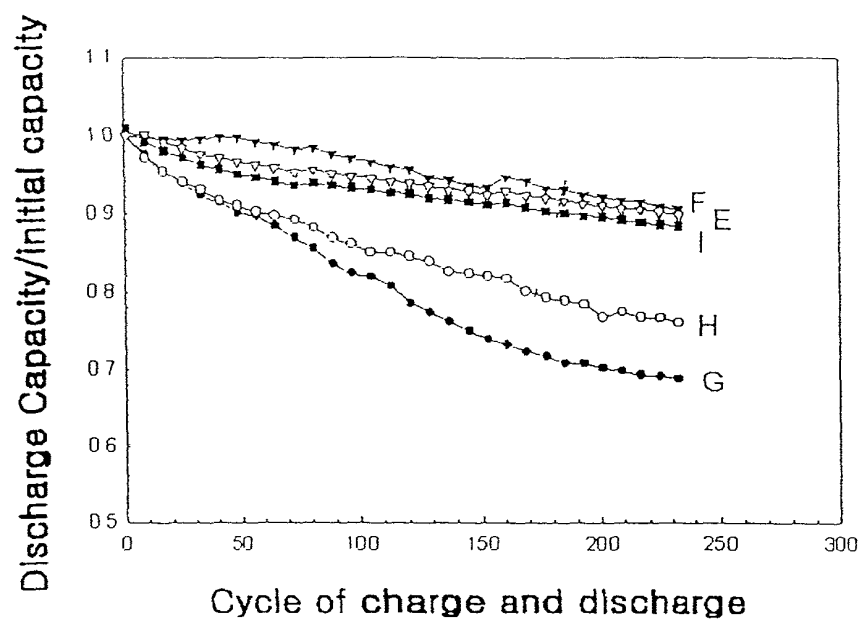


Fig. 3



**MICROPOROUS SOLID ELECTROLYTES AND**  
**METHODS FOR PREPARING THEM**

5    **Technical Field**

10        The present invention relates to an electrolyte film usable in rechargeable cells. More particularly, it relates to a provision of pathways for ions mobile between a cathode and an anode during repeated charge and discharge of rechargeable cells by introducing liquid components and lithium salts (hereinafter, both are referred to as "liquid electrolytes") to an electrolyte film having microporous structures and containing an absorbent.

15        Electrochemical cells include three essential components, i.e., cathode, anode and electrolyte. Examples of materials for said anode are typically compounds in which lithium metal or lithium ions can be intercalated, preferably carbon and polymer materials. Examples of materials for said cathode are typically materials in which lithium ions  
20        can be intercalated. For example, oxide compounds or polymer materials such as lithium cobalt oxide ( $\text{Li}_x\text{CoO}_2$ ), lithium nickel oxide ( $\text{Li}_x\text{NiO}_2$ ), lithium nickel cobalt oxide ( $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$ ), spinel type lithium manganese oxide ( $\text{Li}_x\text{Mn}_2\text{O}_4$ ) and manganese dioxide ( $\text{MnO}_2$ ) can be used. The introduction of a liquid electrolyte to said electrolyte  
25        film can lead to the formation of an ion conductive matrix.

## **Background Art**

Electrochemical cells using polymer electrolytes have some  
5 advantages over ones using liquid electrolytes in that i) they have less  
leakage risk of liquid; ii) they have excellent electrochemical stability,  
which makes it possible to manufacture various types of cells; and iii)  
they make the automation of the manufacturing process easy.

10 Since the fact that polymers such as polyoxyethylene may have  
metal ionic conductivity in case that they contain polar heterologous  
atoms capable of electric interaction with metal ions was found,  
research on ion conductive polymers, i.e., polymer electrolytes has  
been actively conducted. However, since pure polymers such as  
15 polyoxyethylene have very low ionic conductivity of  $10^{-8}$  S/cm or so at  
room temperature, they have a demerit in that they should be  
approached to the temperature of approximately  $100^{\circ}\text{C}$  in order to  
show ionic conductivity of approximately  $10^{-4}$  S/cm applicable to  
electrochemical cells. For this reason, the main stream of the research  
20 on polymer electrolytes was concentrated on the improvement of  
conductivity.

As the fact that the conduction of ion in polymer electrolytes  
requires transfer of polymer chains was found, attempts to improve  
25 conductivity of ions have been carried out in a direction of increasing  
the flexibility of polymer chains. Blonsky *et al* proposed a method for  
manufacturing an electrolyte having increased conductivity of  $10^{-5}$

S/cm by introducing phosphazene linkages to the main chain of the polymers (*J. Am. Chem. Soc.*, 106, 6854 (1984)). However, said electrolyte has lower conductivity and poor mechanical strength.

5           Alternatively, in order to decrease the crystallinity of polymers, various attempts such as modifying the structure of polymers or adding inorganic materials to polymers have been conducted. However, pure polymer electrolytes consisting of polymers and metal salts (not containing liquid electrolytes) still do not exhibit sufficient  
10 conductivity.

On the contrary, gel-type electrolytes disclosed in US Patent 5,219,679 contain liquid electrolytes in their polymer backbones, and thus demonstrate conductivity close to that of liquid electrolytes while  
15 exhibiting properties of polymers in their mechanical properties, suggesting the possibility of commercialization to rechargeable battery. Namely, the cell of said patent doesn't need a separate activation procedure of adding a liquid electrolyte, but contains some amount of liquid electrolytes which were incorporated during the manufacture of  
20 the polymer electrolytes (a mixture of polymer solution and liquid electrolyte was subjected to casting). However, the electrolytes in the US Patent No. 5,219,679 have problems in that they contain polymers such as polyacrylonitrile which are reactive to lithium metal, and thus the reaction products between electrolytes and lithium electrode come  
25 to be accumulated during the storage and use period of the cell, resulting in a constant increase in interfacial resistance.

Meanwhile, Scrosati *et al* manufactured gel-type polymer electrolytes using polymethylmethacrylate having low reactivity with lithium metal (*Electrochim. Acta*, 140, 991 (1995)). These electrolytes which use polymethylmethacrylate as a polymer component have little reactivity with the surface of lithium, and thus have a merit in that the resistance increase phenomenon on the surface of electrode during the storage is insignificant. However, they also have demerits in that they have poor mechanical strength and thus the content of the polymers should be increased to accomplish strength sufficient to form a film, which in turn decreases the conductivity down to  $10^{-4}$  S/cm. In addition, since the gel-type electrolytes contain a large amount of liquid components, it is inevitable that the evaporation of the liquid components on the surface of the electrolytes will occur. For this reason, there have been some risks of causing composition changes due to the loss of liquid components during the storage, which leads to the decrease in conductivity. In addition, this method has a demerit of necessitating a dehumidifying atmosphere wherein moisture is removed to the utmost since lithium salts contained in the liquid electrolytes react and decompose with moisture in the air.

US Patent Nos. 5,296,318 and 5,418,091 proposed a hybrid polymer electrolyte system to compensate for the said problems. This hybrid polymer electrolyte can minimize the moisture effect on the process of manufacturing electrolytes by adding the liquid electrolytes susceptible to the effect of moisture prior to the packaging of battery, while taking advantage of the merits of gel-type polymer electrolytes (the gel-type polymer electrolytes contain a large amount of liquid

electrolytes and thus the conduction of lithium ion proceeds via liquid phase, thereby having similar conductivity to that of liquid electrolytes). However, since the liquid electrolytes are added after electrolyte film is prepared, it is necessary for the inside of the electrolyte film to have  
5 sites capable of absorbing liquid components therein or driving force making the liquid component possible to be penetrated thereinto. To this end, dibutyl phthalate is added as a plasticizer in the step of preparing electrolyte film, and after the assembly of cell is complete, the plasticizer is extracted by the use of an organic solvent such as  
10 alcohol or ether to form sites for liquid component being absorbed. However, due to the procedure of extracting dibutyl phthalate utilizing a chemical reaction, the methods have fatal demerits that the reproducibility is low, manufacturing yield is reduced, and the automation for mass production is difficult.

15 Accordingly, the present inventors in Korean Patent Application No. 98-57030 tried to solve the above-mentioned problems of said prior art by means of adding an absorbent capable of absorbing liquid electrolytes to a polymer matrix to form a solid electrolyte film, and  
20 after the assembly of the battery, introducing a liquid electrolyte to the activation procedure of the battery.

The electrolyte film of the said solid electrolyte consists of an absorbent and a polymer binder under dried condition. The polymer  
25 binder has more or less dense structure. In order to show more excellent lithium ionic conductivity by improving the absorption ability



of a liquid electrolyte, the solid electrolyte of which the stereo structure of the electrolyte film is changed is need.

### **Disclosure of Invention**

5

Accordingly, the present invention desires to solve the above mentioned problems encountered in the process for the preparation of a solid electrolyte which comprise of adding an absorbent capable of absorbing liquid electrolytes to a polymer matrix to form an electrolyte film, and after the assembly of the battery. Namely, the present invention introduces microporous structures to the polymer matrix while maintaining the mechanical strength of the electrolyte film as it is, which facilitates the absorption of the liquid electrolyte, which in turn improves the lithium ionic conductivity of the solid electrolyte.

15

The term “electrolyte film” used in the specification refers to an electrolyte film which is dried condition and does not contain any liquid electrolytes. The term “solid electrolytes” used in the specification means said electrolyte film having ionic conductivity by incorporating liquid electrolytes thereto. Although the solid electrolytes are not in a complete solid state since they contain liquid electrolytes, they are called “solid electrolytes” in order to be distinguished from the liquid electrolytes because the basic backbone of solid electrolytes starts from the electrolyte film at a solid state. In addition, the term “absorbent” used in the specification means materials capable of absorbing liquid electrolytes or of increasing the ability of the solid electrolytes absorbing liquid electrolytes.

The process for assembling batteries refers to binding a cathode and an anode, which are separately prepared, with an interposed electrolyte film in the manner of lamination or pressing. When the electrolyte film is prepared by one of the said methods, liquid electrolytes are added after the assembly of battery, which can minimize the restriction on dehumidifying conditions in the process. Furthermore, according to the present method, the sites capable of absorbing liquid electrolytes are already formed in the course of manufacturing the electrolyte film and thus there is no need for the procedure of extracting a plasticizer. Therefore, the method has some advantages in that it simplifies the process, which not only reduces the production cost but also makes the automation process easy and improves the yield. In addition, when the electrolyte film is prepared by one of the said methods, the polymer matrix comes to have microporous structures, which facilitates the transfer of the liquid electrolyte, which in turn improves the lithium ionic conductivity of the solid electrolyte with the same amount of absorbent.

The solid electrolytes according to the present invention comprise an electrolyte film containing an inorganic absorbent and consisting of microporous structures, and an ion conductive liquid electrolyte.

Said electrolyte film can be preferably prepared by means of a phase inversion method. Examples of such method include wet process

and dry process. The wet process refers to a process for the preparation of an electrolyte film, which comprises the steps of:

dissolving a mixture of an absorbent and a polymer binder in a solvent for the polymer binder,

5 making the resulting solution to a film form,

exchanging the solvent with a non-solvent for the polymer binder, and then

drying the resulting material to form an electrolyte film.

10 On the contrary, the dry process refers to a process for the preparation of an electrolyte film, which comprises the steps of:

mixing a mixture of an absorbent and a polymer binder with a solvent for dissolving the polymer binder, a non-solvent which does not dissolve the polymer binder, a pore former and a wetting agent,

15 making the resulting mixture into a film form, and

drying the resulting film completely.

Subsequently, an activation procedure of absorbing an ion conductive liquid electrolyte into thus prepared porous electrolyte film  
20 may lead to the formation of a solid electrolyte for rechargeable cells.

Accordingly, the solid electrolyte of the present invention can be prepared by introducing an absorbent capable of absorbing the liquid electrolyte or increasing the absorption ability to the inside of the  
25 electrolyte film to form a porous electrolyte film matrix and then injecting an liquid electrolyte thereto. Thus prepared solid electrolyte

has lithium ionic conductivity of approximately  $1 \text{ to } 3 \times 10^{-3} \text{ S/cm}$  at room temperature.

Examples of absorbents capable of absorbing liquid electrolytes or increasing the absorption ability include organic materials such as porous polymers and inorganic materials such as mineral particles.

As porous polymer absorbents, polypropylene, polyethylene, polystyrene and polyurethane to which porosity is introduced by means of net type polymer wherein bulky functional groups are introduced to branched chains or by means of adjusting the parameters of the process according to the present invention can be used. Natural polymers such as wood powder, pulp, cellulose and cork may also be used.

As inorganic absorbents, it is possible to use one or two or more particles selected from the group consisting of mineral particles, synthetic oxide compounds particles and mesoporous molecular sieves. Examples of said mineral particles include mineral particles having phyllosilicate structures such as clay, paragonite, montmorillonite and mica. Examples of said synthetic oxide compounds particles include zeolite, porous silica and porous alumina. Examples of mesoporous molecular sieves include mesoporous molecular sieves made of oxide compounds such as silica/polymer substance and having a pore diameter in 2 to 30 nm. Said mineral particles, synthetic oxide compounds particles and mesoporous molecular sieves may be used in the form of a mixture wherein two or more absorbents selected from the above mentioned absorbents are combined.

Said inorganic absorbents have better mechanical, thermal and electrochemical stability as compared to organic absorbents such as porous polymers, and thus the performance properties of the rechargeable cells utilizing inorganic absorbents are better than those of the rechargeable cells utilizing organic absorbents.

Namely, it was found that when cells are fabricated by assembling an anode and a cathode by means of pressing method or lamination method, the organic absorbents differ from the electrolyte films or polymer binders of composite electrodes in their mechanical and thermal behaviors, and thus the rechargeable cells utilizing these organic absorbents show significant reduction in their discharge capacity during repeated charge and discharge as compared to the rechargeable cells utilizing inorganic absorbents. For example, absorbents consisting of organic materials such as polymers with low melting points or deteriorating mechanical strength may lose their absorption ability in the course of pressing or lamination procedures. In other words, the use of organic absorbents such as polymers may be beneficial to the performance of electrolyte films or solid electrolytes themselves, but it may be very difficult to maintain their original performance when cells are fabricated by means of the pressing or lamination method.

In addition, as explained above, since the transfer of polymer chains directly affects the ionic conductivity in general polymer electrolytes, the effect of temperature on ionic conductivity becomes

significant. Particularly, at low temperatures, the transfer of polymer chains is weakened, which significantly reduces the ionic conductivity, thereby resulting in severe deterioration in the performance of the cells. However, the use of absorbents as in the present invention increases the ionic conductivity. Moreover, if a large amount of inorganic absorbent, which is less affected by temperature, is used, the effect of temperature becomes less unlike the properties of general polymer electrolytes. As a large amount of inorganic absorbent is contained in electrolytes, the electrolytes have some merits in that the resistance against ignition or explosion is improved as compared to the electrolytes containing a large amount of organic material such as polymers.

Accordingly, it can be confirmed that it is preferable to use inorganic absorbents rather than use organic absorbents in the constitution of the electrolyte film of rechargeable cells.

The amount of absorbents added is 30 to 95 % by weight and preferably, 50 to 90 % by weight based on the weight of the dried state electrolyte film which does not contain liquid electrolyte. If the added amount exceeds 95 % by weight, the mechanical strength of the electrolyte film formed falls. If the amount is not more than 30 % by weight, the ability to absorb liquid electrolyte decreases.

The particle size of absorbents is preferably not more than 40  $\mu\text{m}$ , more preferably, not more than 20  $\mu\text{m}$  so as not to decrease the mechanical strength and the uniformity of the electrolyte film.

As polymer binders, it is possible to use most common polymers. Among them, it is preferred to use a mixture of one or two or more polymers selected from the group consisting of copolymers of polyvinylidene fluoride, vinylidene fluoride and hexafluoropropylene, copolymers of vinylidene fluoride and maleic anhydride, polyvinylchloride, polymethylmethacrylate, polymethacrylate, cellulose triacetate, polyurethane, polysulfone, polyether, polyolefine such as polyethylene or polypropylene, polyethylene oxide, polyisobutylene, polybutyldiene, polyvinylalcohol, polyacrylonitrile, polyimide, polyvinyl formal, acrylonitrilebutyldiene rubber, ethylene-propylene-diene-monomer, tetra(ethylene glycol)diacrylate, polydimethylsiloxane, polycarbonate and polysilicon, or copolymers thereof.

The present invention introduces porous structures to the electrolyte film used as a matrix for the solid electrolyte, which facilitates the transfer of liquid electrolyte, and thus improves the lithium ionic conductivity of the solid electrolyte with the use of same amount of absorbent. As methods for preparing said porous electrolyte film include the wet process and dry process, as explained above. The wet process is carried out by subjecting electrolyte film component to a casting and reacting the resulting film with a non-solvent to form microporous structures in the polymer matrix. The dry process is carried out by subjecting the electrolyte film components together with a non-solvent for introducing porosity and a pore former to molding to form a microporous electrolyte film.

As solvents for dissolving polymer binders, a mixture of one or two or more solvents selected from the group consisting of N-methylpyrrolidinone, dimethylformamide, dimethylacetamide, tetrahydrofuran, acetonitrile, cyclohexanone, chloroform, dichloromethane, hexamethylphosphoramide, dimethylsulfoxide, acetone and dioxane.

As non-solvents for the polymer binder, it is possible to use a mixture of one or two or more selected from the group consisting of water, ethanol, ethylene glycol, glycerol, acetone, dichloromethane, ethylacetate, butanol, pentanol, hexanol and ether.

As pore formers, it is preferred to use a mixture of one or two or more selected from the group consisting of 2-propanol, resorcinol, trifluoroethanol, cyclohexanol, hexafluoroisopropanol, methanol and hemiacetal obtained by the reaction of maleic acid with hexafluoroacetone.

As dipping agents, it is preferred to use nonionic surfactants, for example, Triton X-100 (manufactured by Aldrich Company), Igepal DM-710 (manufactured by GAF Company).

The liquid electrolytes, which contain absorbents and are to be absorbed in electrolyte film, can be prepared by dissolving lithium salt in an organic solvent. In the present invention, the absorption of the liquid electrolytes into electrolyte film is defined as "activation".



It is preferred that said organic solvents have high polarity and no reactivity to lithium metal so as to improve the degree of dissociation of ions by raising the polarity of electrolyte and to facilitate ion conduction by lowering local viscosity around ions.

5 Examples of such organic solvents include ethylene carbonate, propylene carbonate, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate,  $\gamma$ -butyrolactone, dimethylsulfoxide, 1,3-dioxane, tetrahydrofuran, 2-methyltetrahydrofuran, sulfolane, N,N-dimethylformamide, diglyme, triglyme and tetraglyme. In particular, it  
10 is preferred that the organic solvent is used in the form of mixed solutions of two or more solvents consisting of high viscosity solvents and low viscosity solvents.

Said lithium salt is preferred to have low lattice energy and a  
15 high degree of dissociation. Examples of such lithium salt include  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSCN}$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  and  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ . The selective mixtures thereof can also be used. The concentration of the lithium salt is preferably 0.5M to 2M.

20 The liquid electrolyte can be added in an amount of 30 to 90 % by weight, preferably 40 to 85 % by weight, based on the total amount of electrolytes including the liquid electrolyte.

The solid electrolyte according to the present invention is  
25 characterized by the facts that it is easy to prepare when compared to prior polymer electrolytes; that it has higher ionic conductivity because the conduction of lithium ions proceeds via liquid phase; and that it is

not affected by moisture or temperature until it absorbs the liquid electrolyte or it is activated.

In the following, the process for the preparation of said solid electrolyte having porous structures is explained in greater detail.

#### Wet process

The solid electrolyte having porous structures according to the present invention can be prepared by five steps, i.e., mixing an absorbent with a polymer binder, dissolution of the resulting mixture, molding, making polymer matrix porous and drying/ activation.

First of all, an absorbent in powder form (particle size of not more than 40  $\mu\text{m}$ ) and a polymer binder are dry mixed in a closed container.

The resulting mixture of the absorbent and the polymer binder is dissolved in a solvent for the polymer binder. The solid content of said mixed solution is preferably 5 to 50 % by weight based on the total weight of the solution. If the content is not more than 5 % by weight, the mechanical strength of the electrolyte film decreases and if the content is more than 50 % by weight, the polymer binder cannot be dissolved sufficiently or the viscosity of the mixed solution becomes large, which is problematic.

In order to facilitate the dissolution of the polymer binder and to avoid the agglomeration between absorbent, a magnetic stirrer, a

mechanical stirrer, a planetary mixer or a high-speed disperser can be used to stir the mixed solution. While stirring, an ultrasonic stirrer may be adopted to prevent the absorbent from agglomerating or bubbling in the middle of mixing. In addition, if desired, the mixed solution may  
5 be subjected to defoaming and filtration steps.

After the polymer binder is completely dissolved and uniformly mixed with the absorbent, the resulting mixture is made in the form of film with a regular thickness. For example, the mixed solution may be  
10 poured on a flat glass plate or a Teflon plate and then be subjected to casting so that the resulting products have a regular thickness. Alternatively, the mixed solution may be extracted from a die with a regular space and then coated onto a substrate made of polymer film. Various other application methods can be selected. It is preferred that  
15 the thickness of the film is controlled in the range of 10 to 200  $\mu\text{m}$ . If the thickness of the film is not more than 10  $\mu\text{m}$ , the mechanical strength decreases, and if the thickness of the film exceeds 200  $\mu\text{m}$ , the ionic conductivity decreases, which is not preferable.

20 After casting in the form of film, in order to introduce porosity to the polymer matrix, the film was contacted with a non-solvent for the polymer binder to extract the solvent for the polymer binder. For example, it is possible to extract the solvent by soaking the film in a non-solvent pool containing a non-solvent. Accordingly, it is preferable  
25 to combine a miscible solvent and a non-solvent. The time for soaking the film in a non-solvent pool varies from one minute to one hour depending on the kinds of the solvents and non-solvents. If the time is

shorter than the defined time, it is difficult to obtain sufficient porosity. On the contrary, if the time exceeds the defined time, the productivity becomes decreased, which is not preferable. The temperature in the pool is preferably from 10°C to 90°C, more preferably from 20°C to 80°C. If the temperature is lower than that, it is difficult to obtain sufficient porosity. If the temperature is excessively high, the mechanical strength of the electrolyte film decreases, which is not preferable. In general, it is preferable to introduce porosity corresponding to the amount of solvents in a mixed solution consisting of an absorbent, a polymer binder and a solvent. It is also preferable to control the composition, temperature and time of the mixed solution so that porosity can be introduced in accordance with the amount of solvents in a mixed solution.

After the extraction of the solvent and completely drying the resulting film, the liquid electrolyte is introduced thereto.

#### Dry process

The solid electrolyte having porous structures according to the present invention can be prepared by dry process consisting of four steps, i.e., mixing an absorbent with a polymer binder, adding additives (solvent, non-solvent, pore former, dipping agent), casting and drying/activation.

An absorbent in powder form (particle size of not more than 40  $\mu\text{m}$ ) and a polymer binder are dry mixed in a closed container. The

resulting mixture of absorbent and the polymer binder is dissolved in a solvent for the polymer binder.

In order to facilitate the dissolution of the polymer binder and to avoid the agglomeration between absorbent, a magnetic stirrer, a mechanical stirrer, a planetary mixer or a high-speed disperser can be used to stir the mixed solution. While stirring, an ultrasonic stirrer may be used to prevent the absorbent from agglomerating or foaming in the middle of mixing. In addition, if desired, the mixed solution may be subjected to defoaming and filtration steps.

After the polymer binder is completely dissolved and uniformly mixed with the absorbent, a solvent which does not dissolve the polymer binder, i.e., a non-solvent is added in an amount range of not causing the precipitation of the polymer binder. In order to facilitate the formation of microporous structures, it is preferable to add pore formers or dipping agents. After said additives are uniformly mixed, the resulting mixture is molded in the form of film with a regular thickness. For example, the mixed solution may be poured on a flat glass plate or a Teflon plate and then be subjected to casting so that the resulting products have a regular thickness. Alternatively, the mixed solution may be extracted from a die with a regular space and then coated onto a substrate made of polymer film. Besides, various other application methods can be selected. It is preferred that the thickness of the film is controlled in the range of 10 to 200  $\mu\text{m}$ . If the thickness of the film is not more than 10  $\mu\text{m}$ , the mechanical strength decreases, and

if the thickness of the film exceeds 200  $\mu\text{m}$ , the ionic conductivity decreases, which is not preferable.

After the completion of making in the form of film, the resulting  
5 electrolyte film is completely dried at 20°C to 200°C and then the liquid electrolyte is introduced thereto.

When compared to the wet process, the dry process has a demerit  
in that the dispersion or mixing of the absorbents, polymer binders and  
10 additives is comparatively difficult. When a complete dispersion or mixing is not conducted, (i) it become difficult to accomplish an even dispersion of pores or absorbents, (ii) it is not easy to cast into the form of an electrolyte film and (iii) the mechanical strength and reproducibility become decrease. Namely, in the event that the pores  
15 or absorbents are dispersed unevenly, it was confirmed that (i) the reaction in cells proceeds non-uniformly localized state when the electrolyte film is used as an electrolyte for electrochemical cells; (ii) the casting in the form of film becomes difficult; and (iii) the mechanical strength decreases, which limited the dry process severely.

20

In addition, the dry process necessitates the addition of non-solvents in order to form pores and in view of the principle of the dry process, the solvent should be evaporated (dried) prior to the non-solvents so that pores can be formed. If the non-solvents are evaporated  
25 prior to the solvents, pores cannot be formed. In this regard, it is essential that the non-solvents should have non-volatile property or higher boiling points than solvents. For this reason, the dry process is

likely to have a problem of residual non-solvents. In other words, non-solvents, which have higher boiling point than solvents or are non-volatile, are difficult to remove completely from the electrolyte film during drying procedure. Therefore, a separate measure (for example, extraction with alcohol or ether or increasing the drying temperature sufficiently) should be taken in order to remove completely the non-solvents. In addition, since said non-solvents are chemically and electrochemically unstable, if said non-solvents remain in the electrolyte film, they may cause side reactions or oxidation or reduction with repeated charge and discharge of cells. As a result, the deterioration of cell performance such as capacity decrease of cells or gas evolution may happen. The same problems apply to the other additives besides non-solvents. It is considered that the process for the preparation of electrolyte film solely consisting of an absorbent and a polymer binder by way of complete removal of additives or the like may be complicated, which render the reproducibility of this process difficult.

Accordingly, it is preferable to prepare the electrolyte films or solid electrolytes by wet process rather than dry process.

The present invention is directed to rechargeable cells, particularly to rechargeable lithium cells wherein said porous solid electrolyte is used as an electrolyte.

The process for assembling batteries refers to binding a cathode and an anode, which are separately prepared, with an interposed

electrolyte film in the manner of lamination, pressing or winding. When the electrolyte film is prepared by one of the said methods, liquid electrolytes are added after the assembly of battery, which can minimize the restriction on dehumidifying atmosphere in the process.

- 5 Furthermore, according to the present method, the sites capable of absorbing liquid electrolytes are already formed in the course of manufacturing the electrolyte film and thus there is no need for the procedure of extracting a plasticizer. Therefore, the method has some advantages in that it simplifies the process, which not only reduces the  
10 production cost but also makes the automation process easy and improves the yield. In addition, when an electrolyte film is prepared by the said method, the polymer matrix comes to have microporous structures, which facilitates the transfer of the liquid electrolyte and improves the lithium ionic conductivity of the solid electrolyte with the  
15 same amount of absorbent.

- In one embodiment of the method for the production of rechargeable cells by the use of the solid electrolyte according to the present invention, a cell can be constructed by bonding a cathode and  
20 an anode, interposed with the porous electrolyte film prepared from the above-mentioned procedure. The porous electrolyte film contains absorbent powder therein and has porous structures, which make the electrolyte film maintain its condition facilitating the absorption of the liquid electrolyte. The cathode is electrically connected to a cathode  
25 current collector; and the anode is electrically connected to an anode current collector. Thus the constructed assembly is activated to be able



to absorb the liquid electrolyte, thereby obtaining an electrochemical cell which is ready to operate.

Fig. 1 illustrates a cross sectional view of the rechargeable cell in which the solid electrolyte according to the present invention is used. The solid electrolyte (1) contains the absorbent powder (11) and the liquid electrolyte, which is absorbed during the activation step. The cathode (2) is electrically connected to a cathode current collector (22) and the anode (3) is electrically connected to an anode current collector (33), respectively.

The procedures for the preparation of the cathode or anode are as follows. The cathode or anode consists of a current collector and an active material layer. The active material layer comprises of active materials, conducting materials and binders, etc. Besides, various additives may be introduced in order to improve the performance of cells. The current collectors, conducting materials, binders and additives, which are contained in the cathode or anode, may be identical or different, depending on desired objectives.

The current collectors provide mobile pathways for electrons, which are generated in the oxidation/reduction reaction, taking place in the cathode or the anode. As current collectors, generally grids, foils, punching foils and etching foils, etc., may be used, depending on the performance or manufacturing processes of the cell. The use of grids can increase the filling rate of the active material, but it may complicate the manufacturing process. The use of foils can improve the

performance of the cell and simplify the manufacturing process, but it may deteriorate the compactness of the active materials. Copper, aluminum, nickel, titanium, stainless steel, carbon, etc., can be used as current collectors. Generally, aluminum is used for the cathode and copper is used for the anode.

The active materials are the most crucial component of electrochemical cells since they determine the performance of cells in view of the fact that the charge and discharge reaction (or oxidation/reduction reaction) of cells take place on these materials. Furthermore, the active materials possess the largest content in the active material layer. As cathode active materials, it is possible to use oxide compounds or sulfide compounds of transition metals, organic compounds, polymer compounds, etc. Preferably, it is possible to use oxide compounds or polymer materials such as lithium cobalt oxide ( $\text{Li}_x\text{CoO}_2$ ), lithium nickel oxide ( $\text{Li}_x\text{NiO}_2$ ), lithium nickel cobalt oxide ( $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$ ), spinel type lithium manganese oxide ( $\text{Li}_x\text{Mn}_2\text{O}_4$ ), manganese dioxide ( $\text{MnO}_2$ ), etc. As anode active materials, alkali metals, alkali earth metals, carbon, oxide compounds or sulfide compounds of transition metals, organic compounds and polymer compounds may be used, preferably carbon or polymer materials can be used. It is essential that the active materials should be chosen in accordance with the desired performance or use of cells.

The conducting materials refer to materials that are added to the cathode or anode in order to improve the electronic conductivity, and are generally carbon. Among them, conducting materials are preferably

graphite, cokes, activated carbon and carbon black, more preferably graphite and carbon black. One or two or more of conducting materials selected from the above group can be used and there is no difference whether they are synthetic or natural materials. The conducting materials are added in an amount of 3 to 15 % by weight based on the total weight of the electrode materials. If the amount of the conducting materials added is not more than 3 % by weight, the electrical conductivity falls, causing the problem of over voltage. If the amount exceeds 15% by weight, the energy density per unit volume decreases and the side reaction due to the conducting materials become severe.

The binders refer to components to be added to enhance the binding ability of the active materials and are generally polymer compounds. The polymer compounds that are used in the preparation of the solid electrolyte film may serve as binders. It is preferable to use binders, which are the same as polymers of the electrolyte film or have miscibility. The binders may be added in an amount of 15 % by weight or less based on the total weight of the electrode materials. If the amount of binders is less than required, the binding ability of the electrodes may decrease. If the amount of binders exceeds 15 % by weight, the processability and porosity of the electrodes decrease.

The additives refer to materials, which are added to improve the performance of cells or electrodes and can be chosen within a wide range in accordance with desired performances or use. The additives are added to improve the binding ability with composite electrodes inside or current collectors, to induce the porosity or non-crystallinity

of the composite electrodes, to improve the dispersibility of the composite electrode constituting materials or the efficiency of the process for the manufacturing of the electrodes, to prohibit the overcharge/overdischarge of the active materials, to recombine or  
5 remove the side reaction products, or to improve the absorption ability of the liquid electrolytes. Generally, salts, organic/inorganic compounds, minerals and polymer compounds can be used as additives, and absorbents added to the electrolyte film can be chosen.

10 In the following, the rechargeable lithium cell according to the present invention will be explained in greater detail.

The porous electrolyte film in a dried solid condition obtained by the above-mentioned process without having the step introducing the  
15 liquid electrolyte is assembled with a cathode and an anode prepared separately to form a cell, to which a liquid electrolyte is absorbed to obtain the rechargeable lithium cell. The solid electrolyte should be subjected to an activation step absorbing the liquid electrolyte in order to have a sufficient ionic conductivity for being used. By passing  
20 through the activation step, the solid electrolyte comes to be workable as an electrochemical cell. In case that the solid electrolyte fails to pass through the activation step, the ionic conductivity at room temperature decreases drastically, which renders the solid electrolyte itself inappropriate as an electrolyte.

25 The process for the preparation of the cathode and/or anode to be assembled with said electrolyte film is as follows. Each mixture of the

cathode or anode materials is kneaded to give slurry. The resulting slurry is made to a thin film by means of casting, coating and screen printing and then the resulting thin film is combined with a current collector by means of pressing or lamination to form a cathode and/or  
5 an anode. Alternatively, the slurry may be directly coated on a current collector to form a cathode and/or an anode.

Onto the surface of the electrodes manufactured by the above mentioned methods a solid electrolyte slurry consisting of an absorbent,  
10 a polymer binder and a solvent may be directly applied to form a cell in which an electrolyte film is formed on the electrodes. Alternatively, one may constitute a cell by lamination or pressing the separately manufactured electrodes and electrolyte film. When a cell is constructed by the former method, the binding ability between the  
15 electrodes and the electrolyte film may increase. However, it will be hard to adopt the former method when the electrodes and the electrolyte film do not correspond with each other, or when the electrodes or the electrolyte film are easy to pollute or lose their performance in the course of manufacturing process. Moreover, in case  
20 that the electrolyte film is prepared by the dry process, electrodes may be contaminated by the non-solvents or pore formers which are used to introduce porous structures, which is problematic. Particularly, when water is used as a non-solvent or a pore former, the cell performance may be deteriorated if water is not completely removed by sufficient  
25 drying step. In addition, there is a problem in that it is very hard to approach the complete drying condition. In the latter method, although there is a demerit in that the binding ability between the electrodes and

the electrolyte film is weak, there are much better merits in that it simplifies the quality control, process design and equipment used. Therefore, the latter method is preferred to the former one.

5       The electrolyte film prepared by the present invention contains an absorbent and thus has advantages in that it has higher mechanical strength as compared to pure electrolyte films or other electrolyte films containing gel type polymer electrolytes or plasticizers. Accordingly, because the electrolyte film of the present invention shows little change  
10 in its shape during the pressing or lamination procedure and has high reproducibility, it has merits in that it can be produced with a low failure rate and on a large scale. Namely, it can be stated that the electrolyte film prepared by the present invention has properties suitable for pressing or lamination methods, which are more  
15 advantageous in terms of quality control, process design and equipment used.

### **Brief Description of Drawings**

20       Figure 1 is a cross sectional view of the cell wherein the solid electrolyte according to the present invention is used.

Figure 2 shows graphs demonstrating the experimental results of linear sweep voltammetry to determine the electrochemical stability of  
25 the solid electrolyte according to the present invention.

Figure 3 shows a variation of discharge capacity of the cell in which the solid electrolyte containing an inorganic absorbent is used as compared to the cell in which polymer absorbent is used with repeated charge and discharge.

5

Drawing Reference Numerals:

- |                      |                               |
|----------------------|-------------------------------|
| 1: solid electrolyte | 11: absorbent powder          |
| 2: cathode           | 22: cathode current collector |
| 3: anode             | 33: anode current collector   |

10

Best Mode for Carrying out the Invention

In the present invention, the solid electrolyte according to the present invention and the process for the preparation of cells by using said solid electrolyte is explained in detail. Firstly, the production of the solid electrolyte and the examination of performances were carried out. In addition, the solid electrolyte is assembled together with the anode and cathode to form a cell and then the procedure to examine the performance of the cell is described. However, the present invention is not restricted to those examples and various modifications are possible within the scope of the invention.

Example 1 (wet process)

An absorbent and PVdF powder were introduced to a 20 *ml* vial and then dry mixed for approximately 5 minutes with a magnetic stirrer. To the resulting mixture 4 *ml* of N-methyl pyrrolidinone was added and then continuously stirred until the binder was completely dissolved. In

order to prohibit the absorbent particles from agglomerating with each other, the resulting solution was further subjected to ultrasonic stirring for 30 minutes while stirring. The mixed solution thus prepared was coated onto a glass plate in thickness of 100  $\mu\text{m}$ . The coated film was soaked in a non-solvent bath for approximately 10 minutes, which was removed from the bath and then dried at 40°C for 1 hour. The porous electrolyte film thus prepared was soaked in a liquid electrolyte solution for approximately 10 minutes. After the liquid electrolyte was completely absorbed, the weight change was determined. The ionic conductivity was also determined by the use of an alternate current impedance method.

Table 1 summarizes the kinds of absorbents and binders, the properties of the porous solid electrolyte in accordance with its content and conductivity. In order to compare the ability of the porous electrolyte film absorbing the liquid electrolyte, sorption capacity ( $\Delta_{\text{ab}}$ ) was defined as follows:

$$\Delta_{\text{ab}} = [\text{amount of the liquid electrolyte absorbed (mg)}] / [\text{weight of the electrolyte film (mg)}]$$

**Table 1**

E x.	Absorbents		PV dF	non- solvent	Liquid Electrolyte	$\Delta_{\text{ab}}$	Ionic Conducti vity mS/cm	Mechani cal strength
	Kind	g	g					
a	Paragonite	0.13	0.28	H <sub>2</sub> O	EC/DMC 1M LiPF <sub>6</sub>	7.0	2.1	Good



b	Paragonite	0.17	0.26	H <sub>2</sub> O	EC/DMC 1M LiPF <sub>6</sub>	6.8	2.2	Good
c	Paragonite	0.72	0.24	H <sub>2</sub> O	EC/PC 1M LiPF <sub>6</sub>	6.9	1.9	Good
d	Paragonite	1.06	0.26	H <sub>2</sub> O	EC/PC 1M LiPF <sub>6</sub>	7.5	1.8	Good
e	Paragonite	1.51	0.26	H <sub>2</sub> O	EC/DMC 1M LiPF <sub>6</sub>	8.0	2.4	Good
f	Paragonite	2.00	0.26	H <sub>2</sub> O	EC/DMC 1M LiPF <sub>6</sub>	8.5	2.5	Good
g	Paragonite	1.98	0.25	Ethanol	EC/DMC 1M LiPF <sub>6</sub>	5.1	1.0	Good
h	Zeolite	1.37	0.60	H <sub>2</sub> O	EC/DMC 1M LiPF <sub>6</sub>	7.2	1.9	Good
i	Zeolite	1.50	0.38	H <sub>2</sub> O	EC/DMC 1M LiPF <sub>6</sub>	8.2	2.0	Good
j	Zeolite	1.65	0.29	H <sub>2</sub> O	EC/DMC 1M LiPF <sub>6</sub>	8.0	2.4	Good
k	Montmorillonite	1.34	0.58	H <sub>2</sub> O	EC/DMC 1M LiPF <sub>6</sub>	8.0	2.8	Good
l	Montmorillonite	1.50	0.38	H <sub>2</sub> O	EC/DMC 1M LiPF <sub>6</sub>	8.2	2.9	Good
m	Porous Silica	1.35	0.59	H <sub>2</sub> O	EC/DMC 1M LiPF <sub>6</sub>	8.5	2.4	Good
n	Polypropylene	1.35	0.60	H <sub>2</sub> O	EC/DMC 1M LiPF <sub>6</sub>	7.0	1.9	Good
o	Wood powder	1.35	0.60	H <sub>2</sub> O	EC/DMC 1M LiPF <sub>6</sub>	7.4	2.0	Good

### Example 2 (wet process)

5 Paragonite powder and a binder powder were introduced to a 20 *ml* vial and then dry mixed for approximately 5 minutes with a magnetic stirrer. To the resulting mixture 4 *ml* of N-methyl pyrrolidinone was added and then continuously stirred until the binder was completely dissolved. In order to prohibit the absorbent particles

10 from agglomerating with each other, the resulting solution was further subjected to ultrasonic stirring for 30 minutes while stirring. The mixed solution thus prepared was coated onto a glass plate in thickness of 100  $\mu\text{m}$ . The coated film was soaked in a water bath for 10 minutes, which was removed from the bath and then dried at 40°C for

15 approximately one hour. The porous electrolyte film thus prepared was

soaked in a liquid electrolyte solution for approximately 10 minutes. After the liquid electrolyte was completely absorbed, the weight change was determined. The ionic conductivity was also determined by the use of an alternate current impedance method. The results are summarized in Table 2.

**Table 2**

E x.	Paragonite	Binder		Liquid Electrolyte	$\Delta_{ab}$	Ionic Conducti vity mS/cm	Mechani cal strength
	g	Kind	g				
a	1.98	PVdF	0.24	EC/DMC 1M LiPF <sub>6</sub>	8.1	2.4	Good
b	2.00	P(VdF-HFP)	0.26	EC/DMC 1M LiPF <sub>6</sub>	8.0	2.6	Good
c	1.95	PAN	0.25	EC/DMC 1M LiPF <sub>6</sub>	7.8	2.2	Good
d	2.00	PU	0.26	EC/DMC 1M LiPF <sub>6</sub>	8.9	2.9	Good
e	1.98	PVC	0.25	EC/DMC 1M LiPF <sub>6</sub>	7.4	2.0	Good
f	2.00	P(VdF-HFP)	0.26	EC/DMC 1M LiPF <sub>6</sub>	8.5	2.5	Good

### Example 3 (dry process)

1.17 g of paragonite and 0.5 g of P(VdF-HFP) were introduced to a 20 ml vial and then dry mixed for approximately 5 minutes with a magnetic stirrer. To the resulting mixture 8 g of acetone was added and then continuously stirred until the binder was completely dissolved. In order to prohibit the absorbent particles from agglomerating with each other, the resulting solution was further subjected to ultrasonic stirring for 30 minutes while stirring. To the resulting mixed solution 0.9 g of ethylene glycol, 0.1 g of Triton X-100 and 1.8 g of isopropanol were added and then the resulting mixture was subjected to ultrasonic

stirring for approximately 10 minutes until the added mixture was uniformly mixed. The mixed solution thus prepared was coated onto a glass plate in thickness of 100  $\mu\text{m}$ . The coated film was dried at 40°C for approximately 2 hours, which was further dried for approximately 6  
5 hours in a vacuum drier set to 50°C. The electrolyte film thus prepared was soaked in an EC/DEC 1M  $\text{LiPF}_6$  solution for approximately 10 minutes. After the liquid electrolyte was completely absorbed, the weight change was determined.  $\Delta_{\text{ab}}$  value measured by the use of the weight change was 7.5. The conductivity determined at room  
10 temperature by an alternate current impedance method was  $2.0 \times 10^{-3}$  S/cm.

#### Example 4 (Comparative Example)

15 2 g of paragonite and 0.26 g of PVdF were introduced to a 20 *ml* vial and then dry mixed for approximately 5 minutes with a magnetic stirrer. To the resulting mixture 4 *ml* of N-methyl pyrrolidinone was added and then continuously stirred until the binder was completely dissolved. In order to prohibit the absorbent particles from  
20 agglomerating with each other, the resulting solution was further subjected to ultrasonic stirring for 30 minutes while stirring. The mixed solution thus prepared was coated onto a glass plate in thickness of 100  $\mu\text{m}$ . The coated film was dried at room temperature for approximately 2 hours and then was further dried for 6 hours in a  
25 vacuum drier. The temperature of the vacuum drier was controlled to approximately 50°C. The present example differs from Examples 1 to 3 in the fact that a process for forming porous structures was not

conducted. The electrolyte film thus prepared was soaked in a liquid electrolyte solution for approximately 10 minutes. After the liquid electrolyte was completely absorbed, the weight change was determined. The conductivity was determined by the use of an alternate  
5 current impedance method. Lithium ionic conductivity measured at room temperature was  $7.0 \times 10^{-4}$  S/cm.

### Example 5

10 In order to determine the electrochemical stability of the porous solid electrolyte, the linear sweep voltammetry method was carried out by the use of a stainless steel (#304) as an operating electrode and lithium metal as an opposite electrode and a standard electrode. The electrochemical voltage applied in the linear sweep voltammetry was  
15 from an open circuit voltage to 5.5V. The scan rate of the linear sweep voltammetry was 10mV/sec. The results of the linear sweep voltammetry measured on the porous solid electrolyte prepared by the methods of Example 1-(f), 1-(j), 1-(l) and 2-(s) are shown as A, B, C and D, respectively, in Fig. 2.

20

### Example 6

In order to determine the performances of the cell using the solid electrolyte, an oxide compound cathode, a carbon anode and a solid  
25 electrolyte according to the present invention were assembled to fabricate cells, and then the charge and discharge test on thus fabricated cells was carried out. The fabricated cells were in a laminated form and

were prepared by lamination of the cathode, anode and electrolyte film to form an assembly, to which a liquid electrolyte was absorbed. The constant current was applied with a rate charging the reversible capacity within 2 hours (C/2 rate) until the cell voltage became 4.2 V, and then the constant voltage of 4.2 V was applied again until the current decreased down to C/10 mA. Subsequently, the discharging current was applied with a rate discharging the voltage down to 2.5 V or 2.75 V within 2 hours (C/2 rate). The charge and discharge experiment was repeated and the change of discharge capacity with the charge and discharge was measured. The cell constitution and the test results are summarized in the following Table 3 and shown in Fig. 3. As listed in Table 3, the solid electrolyte refers to the conditions where a liquid electrolyte is absorbed into an electrolyte film. In addition, the solid electrolyte obtained in Example 4 was not applied for cell tests.

**Table 3**

Ex.	Cathode				Anode				Solid Electrolyte	Fig.
	Active material	Conducting material	Binder	Additive	Active material	Conducting material	Binder	additive		
v	LiCoO <sub>2</sub>	Carbon black	PVdF	Paragonite	Graphite	Carbon black	PVdF	Paragonite	Ex. 1-(e)	Fig.3-E
w	LiCoO <sub>2</sub>	Carbon black	PVdF	Zeolite	Graphite	Carbon black	PVdF	Zeolite	Ex.1-(j)	Fig.3-F
x	LiCoO <sub>2</sub>	Carbon black	PVdF	Zeolite	Graphite	Carbon black	PVdF	Zeolite	Ex.1-(n)	Fig.3-G
y	LiCoO <sub>2</sub>	Carbon black	P(VdF-HFP)	Zeolite	Graphite	Carbon black	P(VdF-HFP)	Zeolite	Ex.3	Fig.3-H
z	LiMn <sub>2</sub> O <sub>4</sub>	Carbon black	P(VdF-HFP)	Paragonite	Graphite	Carbon black	P(VdF-HFP)	Paragonite	Ex.2-(q)	Fig.3-I

Fig.3 illustrates the discharge capacity with repeated charge and discharge of the cell obtained by the respective examples in comparison with the first discharge capacity. From the test results, it was confirmed that the use of the solid electrolytes containing inorganic absorbents (Examples 6-v, w, z) shows much better cell performances than that of the solid electrolyte containing organic absorbents such as polymers (Example 6-x). Furthermore, it was also confirmed that the use of solid electrolytes obtained by the wet process according to the present invention (Examples 1 and 2) shows much better cell performances than that of the solid electrolyte obtained by the dry process (Example 6-y). Namely, the solid electrolyte containing inorganic absorbent and prepared by the wet process has a much better effect on the total cell performances (charge and discharge performance, etc.), although the electrolyte film or solid electrolyte itself does not show any significant differences in properties (ionic conductivity, mechanical strength, etc.).

### **Industrial Applicability**

The microporous solid electrolytes according to the present invention are characterized by the following facts:

they have high mechanical strength, which makes them suitable to be made into thin films;

they have high ionic conductivity corresponding to that of the liquid electrolytes since the microporous structures and absorbents

introduced to the polymer matrix facilitate the absorption of the liquid electrolyte and there is no restriction on the transfer of lithium ions;

unlike general polymer electrolytes in gel type, they do not require any particular dehumidifying atmosphere since lithium salt,  
5 which is easily decomposed by a trace amount of moisture, is not introduced during the manufacturing of the electrolyte films;

they have a broad electrochemical potential window since the absorbent therein is electrochemically stable; and

they are of ease in automation for mass production due to the  
10 simple process for the production of the electrolyte.

In addition, it is possible for the microporous solid electrolyte according to the present invention to minimize the surface resistance between the electrolyte and electrodes since the binding ability with the  
15 cathode and anode is excellent and the volume change due to the introduction of the liquid electrolyte is little. Therefore, the microporous solid electrolyte according to the present invention is suitable for being used as an electrolyte for rechargeable lithium cells. The solid electrolytes containing inorganic absorbents also show  
20 superior mechanical, thermal and electrochemical stability to those of the solid electrolytes containing organic absorbents, thereby showing less decrease in their discharge capacity during the repeated charge and discharge. When introducing porous structures to the electrolyte, the wet process is more efficient and stable than the dry process. The  
25 microporous solid electrolyte shows superior performances such as less decrease in their discharge capacity as mentioned above when they are used to form electrochemical cells.



**WHAT IS CLAIMED IS:**

1. A solid electrolyte for rechargeable cells, comprising:

5 an electrolyte film having a thickness of 10 to 200  $\mu\text{m}$  and microporous structures; and

an ion conductive liquid electrolyte in an amount of 30 to 90 % by weight based on the total weight of the electrolyte including liquid electrolyte,

10 wherein said electrolyte film contains an absorbent having a particle size not more than 40  $\mu\text{m}$  in an amount of 30 to 95 % by weight based on the total weight of the electrolyte film under the dried condition that no liquid electrolyte is contained therein.

15 2. A solid electrolyte for rechargeable cells according to Claim 1, in which said electrolyte film is prepared by the wet process comprising the steps of:

dissolving a mixture of an absorbent and a polymer binder in a solvent for the polymer binder,

20 making the resulting solution into a film,

exchanging the solvent with a non-solvent for the polymer binder, and then drying the resulting material.

25 3. A solid electrolyte for rechargeable cells according to Claim 1, in which said electrolyte film is prepared by the dry process comprising the steps of:

dissolving a mixture of an absorbent and a polymer binder in a solvent for the polymer binder,

adding a non-solvent for the polymer binder, a pore former and a dipping agent to the resulting solution, and

5 making the resulting solution into a film and then drying the resulting film.

4. A solid electrolyte for rechargeable cells according to Claim 2 or Claim 3, in which

10 said solid electrolyte is prepared by an activation procedure in which an ion conductive liquid electrolyte is absorbed into said electrolyte film, and

said ion conductive liquid electrolyte is obtained by dissolving one or two or more lithium salts selected from the group consisting of  
15  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSCN}$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  and  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$  in a mixture of one or two or more organic solvents selected from the group consisting of ethylene carbonate, propylene carbonate, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate,  $\gamma$ -butyrolactone, 1,3-dioxane, tetrahydrofuran, 2-methyltetrahydrofuran,  
20 dimethylsulfoxide, sulfolane, N,N-dimethylformamide, diglyme, triglyme and tetraglyme in a concentration of 0.5M to 2M.

5. A solid electrolyte for rechargeable cells according to Claim 2 or Claim 3, in which

25 said absorbent is a mixture of one or two or more selected from the group consisting of porous polymer particles such as polyethylene, polypropylene, polystyrene, polyurethane, pulp, cellulose, cork and

wood powder; mineral particles such as clay, paragonite, montmorillonite and mica; synthetic oxide compounds particles such as zeolite, porous silica and porous alumina; mesoporous molecular sieves having 2 to 30 nm of pore diameter made of oxide compounds or  
5 polymers; and other commercially available absorbents;

said polymer binder is a mixture of one or two or more selected from the group consisting of copolymers of polyvinylidene fluoride, vinylidene fluoride and hexafluoropropylene, copolymers of vinylidene fluoride and maleic anhydride, polyvinylchloride,  
10 polymethylmethacrylate, polymethacrylate, cellulose triacetate, polyurethane, polysulfone, polyether, polyethylene, polypropylene, polyethylene oxide, polyisobutylene, polybutylidene, polyvinylalcohol, polyacrylonitrile, polyimide, polyvinyl formal, acrylonitrilebutyldiene rubber, ethylene-propylene-diene-monomer, tetraethyleneglycol  
15 diacrylate, polydimethylsiloxane, polycarbonate and silicon polymer, or their copolymer;

said solvent for dissolving polymer binders is a mixture of one or two or more solvents selected from the group consisting of N-methylpyrrolidinone, dimethylformamide, dimethylacetamide,  
20 tetrahydrofuran, acetonitrile, cyclohexanone, chloroform, dichloromethane, hexamethylphosphoramide, dimethylsulfoxide, acetone and dioxane; and

said non-solvent for the polymer binders is a mixture of one or two or more selected from the group consisting of water, ethanol,  
25 ethylene glycol, glycerol, acetone, dichloromethane, ethylacetate, butanol, pentanol, hexanol and ether.

6. A solid electrolyte for rechargeable cells according to Claim 5, in which said absorbent is a mixture of one or two or more selected from the group consisting of mineral particles, synthetic oxide compounds particles and mesoporous molecular sieves.

5

7. A lithium rechargeable cell, which is obtained by the following steps of:

dissolving a mixture of an absorbent and a polymer binder in a solvent for the polymer binder,

10 making the resulting solution into a film,

exchanging said solvent with a non-solvent for the polymer binder and drying it to form a microporous electrolyte film containing the absorbent,

15 assembling the resulting electrolyte film together with a cathode and an anode separately prepared to form a cell, and then

subjecting the resulting cell to absorb an ion conductive liquid electrolyte.

1098327.00504

## ABSTRACT

### [Summary]

The present invention relates to a solid electrolyte having a good conductivity to lithium ion by allowing the liquid components and lithium salts to be absorbed into the electrolyte film containing an absorbents added at the time of its preparation and having a porosity, a process for preparing the same and a rechargeable lithium cell using the same as an electrolyte. As the absorbent, inorganic materials having not more than 40  $\mu\text{m}$  of particle size can be used. As the polymer binder, any binder of whom solubility against the liquid electrolyte is small can be used. A wet process can introduce the porous structure of the electrolyte film. The solid electrolyte according to the present invention has the ionic conductivity of more than approximately  $1$  to  $3 \times 10^{-3}$  S/cm at room temperature and low reactivity to lithium metal. The cell is fabricated from the solid electrolyte together with electrodes by lamination or pressing methods and, the liquid electrolyte, which is decomposed by moisture, is introduced to a cell just before packaging. Therefore, the solid electrolyte according to the present invention is not affected by the humidity and temperature conditions during the manufacturing of the electrolyte film. In addition, the solid electrolyte according to the present invention has high thermal, mechanical and electrochemical stability, and thus is suitable as an electrolyte for rechargeable lithium cells.

### [Representative Drawing]

Fig. 2

FOIA b 7 - EXEMPT

EL632175763US  
09/868227

# Drawings

Fig. 1

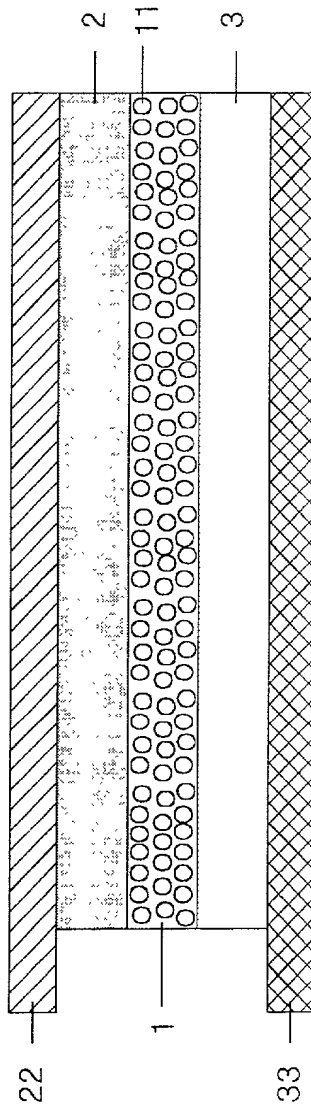


Fig. 2

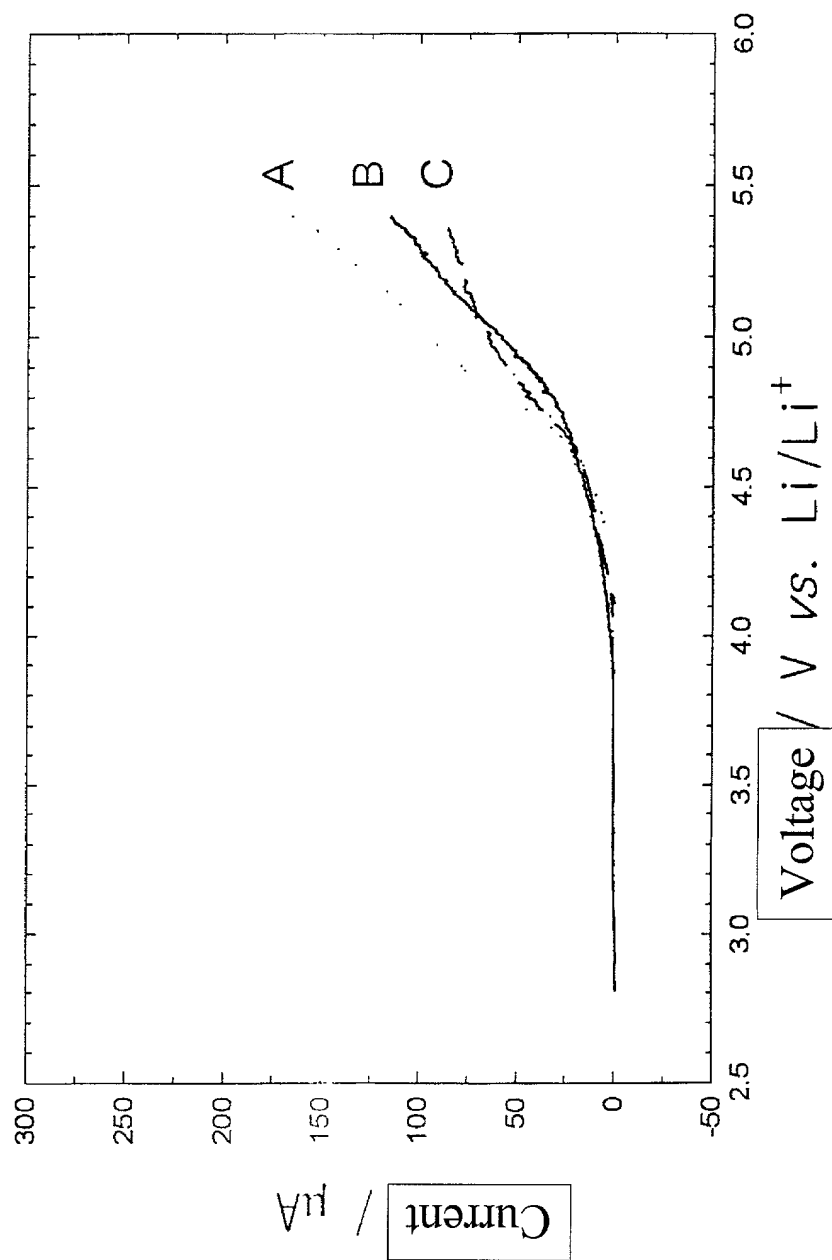
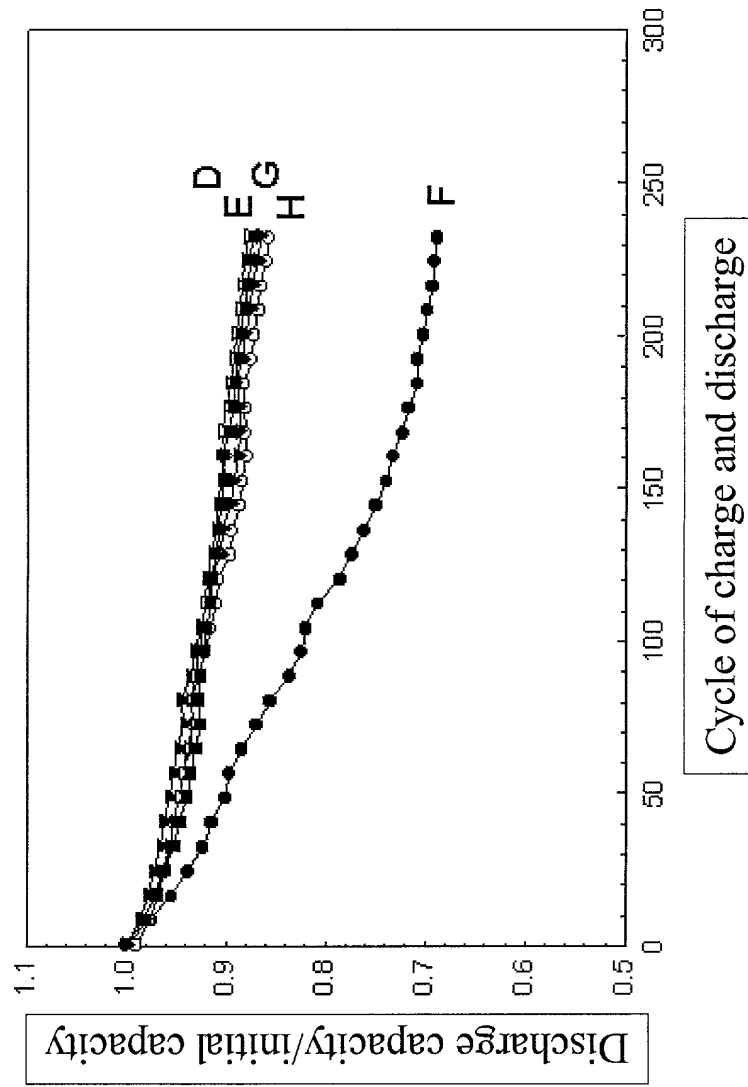


Fig. 3





Attorney's Docket No. B-4208PCT 618872-5

### COMBINED DECLARATION AND POWER OF ATTORNEY

(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL, CONTINUATION, OR CIP)

As a below named inventor, I hereby declare that:

#### TYPE OF DECLARATION

This declaration is of the following type: (check one applicable item below)

- ☒ [ X ] original  
☐ [ ] design  
☐ [ ] supplemental

NOTE: If the declaration is for an International Application being filed as a divisional, continuation or continuation-in-part application, do not check next item; check appropriate one of last three items.

- ☒ [ X ] national stage of PCT

NOTE: If one of the following 3 items apply, then complete and also attach ADDED PAGES FOR DIVISIONAL, CONTINUATION, OR CIP.

- ☐ [ ] divisional  
☐ [ ] continuation  
☐ [ ] continuation-in-part (CIP)

#### INVENTORSHIP IDENTIFICATION

WARNING: If the inventors are each not the inventors of all the claims an explanation of the facts, including the ownership of all the claims at the time the last claimed invention was made, should be submitted.

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

#### TITLE OF INVENTION

**"MICROPOROUS SOLID ELECTROLYTES AND METHODS FOR PREPARING THEM"**

#### SPECIFICATION IDENTIFICATION

the specification of which: (complete (a), (b) or (c))

- (a) ☐ [ ] is attached hereto.  
 (b) ☒ [ X ] was filed on \_\_\_\_\_ as ☒ [X] U.S. Serial No. 09 /868,227  
 or ☐ [ ] Express Mail No., as Serial No. not yet known, \_\_\_\_\_  
 and was amended on \_\_\_\_\_ (if applicable).

NOTE: Amendments filed after the original papers are deposited with the PTO which contain new matter are not accorded a filing date by being referred to in the declaration. Accordingly, the amendments involved are those filed with the application papers or, in the case of a supplemental declaration, are those amendments claiming matter not encompassed in the original statement of invention or claims. See 37 CFR 1.67.

- (c) ☒ [ X ] was described and claimed in  
 PCT International Application No. PCT/KR99/00798 ✓  
 filed on 21 December 1999 as amended under PCT Article 19 (1)  
 on \_\_\_\_ (if any).

## ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code Federal Regulations § 1.56.

☐ In compliance with this duty there is attached an information disclosure statement 37 CFR 1.97.

### PRIORITY CLAIM

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign applications(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

(complete (d) or (e))

(d) ☐ no such applications have been filed.

(e) ☒ such applications have been filed as follows.

*NOTE: Where item (c) is entered above and the International Application which designated the U.S. claimed priority check item (e), enter the details below and make the priority claim.*

### EARLIEST FOREIGN APPLICATION(S), IF ANY, FILED WITHIN 12 MONTHS (6 MONTHS FOR DESIGN(S)) PRIOR TO THIS U.S. APPLICATION

COUNTRY	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 37 USC 119
KOREA ✓	1998/57031 ✓	22 December 1998 ✓	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

### ALL FOREIGN APPLICATION(S), IF ANY FILED MORE THAN 12 MONTHS (6 MONTHS FOR DESIGN(S)) PRIOR TO THIS U.S. APPLICATION

POWER OF ATTORNEY

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration number)

8 - Richard P. Berg, Reg. No. 28,145  
Mavis S. Gallenson, Reg. No. 32,464  
Kam C. Louie, Reg. No. 33,008  
Ross A. Schmitt, Reg. No. 42,529

Victor Repkin, Reg. No. 45,039  
John Palmer, Reg. No. 36,885  
Peter D. Galloway, Reg. No. 27, 885  
William R. Evans, Reg. No. 25, 858

(check the following item, if applicable)

[ ] Attached as part of this declaration and power of attorney is the authorization of the above-named attorney(s) to accept and follow instructions from my representative(s).

SEND CORRESPONDENCE TO:

DIRECT TELEPHONE CALLS TO:

(Name and telephone number)

Mavis S. Gallenson, Esq.  
c/o LADAS & PARRY  
5670 Wilshire Boulevard, Suite 2100  
Los Angeles, California 90036-5679

Mavis S. Gallenson  
(323) 934-2300

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

1-00 Full name of sole or first inventor Dong Hun JANG  
Inventor's signature X *Dong Hun JANG*  
Date X 2001. 7. 24 Country of Citizenship REPUBLIC OF KOREA  
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2-00 Full name of second joint inventor, if any Sa Heum KIM  
Inventor's signature X *Sa Heum KIM*  
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Residence 103-401, Maehwa Jugong Apt., Yatap-Dong, Pundang-Gu,  
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Post Office Address (same as residence)

400 Full name of **fourth joint inventor**, if any Sung Min HONG  
Inventor's signature [Signature]  
Date 2001.07.24 Country of Citizenship REPUBLIC OF KOREA ✓  
Residence 104-1101, Oksoo Hights Apt., Oksoo-Dong, Sungdong-Gu, Seoul,  
133-100, Republic of Korea XXX  
Post Office Address (same as residence)

(Declaration and Power of Attorney - Page 4 of 5)

**CHECK PROPER BOX(ES) FOR ANY OF THE FOLLOWING ADDED PAGES(S)  
WHICH FORM A PART OF THIS DECLARATION**

- ☒ Signature for third and subsequent joint inventors. *Number of pages added* 1
- ☐ Signature by administrator(trix), executor(trix) or legal representative for deceased or incapacitated inventor. *Number of pages added* \_\_\_\_\_
- ☐ Signature for inventor who refuses to sign or cannot be reached by person authorized under 37 CFR 1.47. *Number of pages added* *Added pages to combined declaration and power of attorney for divisional, continuation-in-part (CIP) application.*  
*Number of pages added* \_\_\_\_\_

\* \* \*

- ☐ Authorization of attorney(s) to accept and follow instructions from representative.

\* \* \*

***If no further pages form a part of this Declaration then end this Declaration with this page and check the following item.***

- ☒ This declaration ends with this page.

Applicant or Patentee: Dong Hun JANG, et al. Attorney's Docket No.: B-4208PCT 618872-5  
 U.S. Serial or U.S. Patent No.: 09/868,227  
 Filed or Issued: \_\_\_\_\_  
 International Application No. PCT/KR99/00798, filed 21 December 1999  
 For: "MICROPOROUS SOLID ELECTROLYTES AND METHODS FOR PREPARING THEM"

**VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS**  
**37 CFR 1.9(F) AND 1.27(c) - SMALL BUSINESS CONCERN**

I hereby declare that I am:

☐ the owner of the small business concern identified below:  
☒ an official of the small business concern empowered to act on behalf of the concern identified below:

Name of Concern: Finecell Co., Ltd.

Address of Concern: Room No. Gongjang-Dong 405, Jungahng Induspia, 517-13 Sangdaewon 1-Dong, Jungwon-Gu, Sungnam-City, Gyeonggi-Do, 462-806, REPUBLIC OF KOREA

I hereby declare that the above identified small business concern qualifies as a small business concern as defined in 13 CFR 121.3-18, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees under Section 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention, entitled: "MICROPOROUS SOLID ELECTROLYTES AND METHODS FOR PREPARING THEM" by inventor(s): Dong Hun Jang, Sa Heum KIM, Han Jun KIM, and Sung Min HONG described in:

☐ the specification filed herewith.  
☒ application serial no.: 09/868,227, filed \_\_\_\_\_.  
☒ International Application No. PCT/KR99/00798, filed 21 December 1999.

If the rights held by the above identified small business concern are not exclusive, each individual, concern or organization having rights to the invention is listed below\*, and no rights to the invention are held by any person, other than the inventor, who could not qualify as a small business concern under 37 CFR 1.9(c) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a non-profit organization under 37 CFR 1.9(e). \*NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

FULL NAME \_\_\_\_\_  
 ADDRESS \_\_\_\_\_

☐ INDIVIDUAL ☐ SMALL BUSINESS CONCERN ☐ NONPROFIT ORGANIZATION

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS  
37 CFR 1.9(F) AND 1.27(c) - SMALL BUSINESS CONCERN

(PAGE 2)

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. [37 CFR 1.28(b)]

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

Name of Person Signing: Dong Hun Jang

Title of Person Other Than Owner: Chief Executive Officer

Address of Person Signing: Singnam city, Gyunggido, KOREA

Signature: Donghun Jang

Date: 2001. 7. 24

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant(s): Dong Hun JANG, et al.

Re: SUBMITTAL OF VERIFIED STATEMENT  
CLAIMING SMALL ENTITY STATUS

U.S. Serial No.: 09/868,227

Group Art Unit: not yet assigned

INTERNATIONAL APPLICATION NO.:

PCT/KR99/00798

INTERNATIONAL FILING DATE:

21 December 1999

Our Ref.: B-4208PCT 618872-5

For: "MICROPOROUS SOLID ELECTROLYTES  
AND METHODS FOR PREPARING THEM"

Date: September 5, 2001

Commissioner for Patents  
BOX PCT  
United States Patent and Trademark Office  
Washington, D.C. 20231

Attn: Winston M. Alvarado  
U.S. National Stage Processing  
PCT International Division

Dear Mr. Alvarado:

Enclosed for filing in the subject application is the executed Verified Statement Claiming Small Entity Status (Small Business Concern) signed by Dong Hun Jang, Chief Executive Officer of Finecell Co., Ltd.

Respectfully submitted,



Mavis S. Gallenson  
Attorney for Applicant  
Reg. No. 32,464  
LADAS & PARRY  
5670 Wilshire Boulevard  
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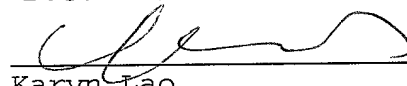
Encl: Verified Statement Claiming Small Entity Status--Small Business Concern

**CERTIFICATION UNDER 37 CFR 1.10**

I hereby certify that this paper and the documents referred to as enclosed therein are being deposited with the United States Postal Service in an Express Mail envelope with sufficient postage for Express Mailing on this date September 5, 2001 in an envelope as "Express Mail Post Office to Addressee" Mailing Label Number EL915795298US addressed to the:

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Date: September 5, 2001

  
Karyn Lao